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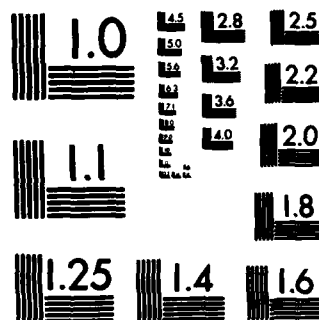
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SOLVATION AND DIELECTRIC DISPERSION IN OPTICAL ELECTRON TRANSFER

by

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and a fixed nuclear configuration of the solvent. The following interaction energies are considered: charge-induced dipole, dipole-induced dipole, induced dipole-induced dipole, formation of induced dipoles, solute-solvent London dispersion, solvent-solvent London dispersion, solute-solvent and solvent-solvent Born repulsion. The change of solvation free energy in aqueous solution is computed in the 7 to 11 eV range from data on the refractive index of water obtained by reflectance spectroscopy. The theory accounts quantitatively for the effect of dispersion on photoelectron emission by aqueous solutions of anions, cations and molecules.



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Solvation and dielectric dispersion in optical electron transfer

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The effect of dielectric dispersion of the solvent on the energetics of optical electron transfer is determined quantitatively by variations of the free energy of solvation of the species being photoionized. The solvation free energy varies because the solvent polarizability in the inner-sphere region of the photon absorbing species changes with photon energy on account of dispersion. The solvation free energy is computed for a varying polarizability of the solvent in the inner-sphere region and a fixed nuclear configuration of the solvent. The following interaction energies are considered: charge-induced dipole, dipole-induced dipole, induced dipole-induced dipole, formation of induced dipoles, solute-solvent London dispersion, solvent-solvent London dispersion, solute-solvent and solvent-solvent Born repulsion. The change of solvation free energy in aqueous solution is computed in the 7 to 11 eV range from data on the refractive index of water obtained by reflectance spectroscopy. The theory accounts quantitatively for the effect of dispersion on photoelectron emission by aqueous solutions of anions, cations and molecules.

I. INTRODUCTION

Photoionization of ions and molecules in aqueous solutions occurs at photon energies (UV and vacuum UV) at which the optical dielectric constant ϵ_{op} of the solvent differs from the limiting value in the visible range ϵ_{op}^0 ($= 1.777$ at 25°C) on account of dielectric dispersion. This change from ϵ_{op}^0 to ϵ_{op} affects the water molecules in the inner-sphere solvation shell of the species being photoionized. The free energy of hydration of the ion or molecule absorbing a photon is changed as a result of

dispersion, as was recently pointed out,¹ and the free energy of photoionization varies accordingly. This change of free energy was derived in Ref. 1 by application of the Marcus theory of nonequilibrium polarization of a continuous medium² to the inner-sphere solvation shell. The resulting equation was shown to account reasonably well for the effect of the variation of ϵ_{op} with photon energy on the photoelectron emission by aqueous solutions of 17 different inorganic anions in the 7 to 10 eV range.

The Marcus theory² is formulated in terms of the macroscopic concept of polarization, and its application to the inner-sphere solvation shell is more tentative than the usual justified application to outer-sphere reorganization. It seemed advisable therefore to develop a theory based on a discrete number of water molecules in the inner-sphere region. This is done in the present paper on the basis of ideas developed in the treatment of ionic hydration.³⁻⁵ This new approach is also more detailed than the one in Ref. 1 as it includes consideration of London dispersion energies and the interpretation of the effect of dielectric dispersion on the photoionization of electrically neutral molecules. The new theory agrees very well with experiment.

II. FREE ENERGY OF OPTICAL ELECTRON TRANSFER WITH VARYING SOLVENT POLARIZABILITY

A. Free energy of optical electron transfer as a function of solvent polarizability

The treatment is divided into two parts. Firstly, it will be shown that the free energy characterizing the optical electron transfer is related directly to the free energy of solvation of the species being photoionized. Secondly, this solvation free energy will be computed for a varying polarizability of the solvent and a fixed nuclear configuration of the solvent. The argument is developed for photoelectron emission by solutions but is of general validity for optical electron transfer.

Consider the photoelectron emission into the vapor phase by an aqueous solution of ions or molecules denoted by C. This process is characterized by a free energy of emission ΔG_m which will be related to the solvation free energy of the species C. The change of free energy between the initial and final states of the emission process is obtained from the following sequence where the symbols (aq) and (g) denote the liquid and gas phase, respectively: $C(aq) = C(g)$; $C(g) = C^+(g) + e^-(g)$; $C^+(g) = C^+(aq)$. The free energy of emission ΔG_m is,⁶

$$\Delta G_m = I + \Delta G_s(C^+) - \Delta G_s(C) + R + |e|\chi, \quad (1)$$

where I is the ionization potential of C(g); $\Delta G_s(C^+)$ and $\Delta G_s(C)$ are free energies of solvation; R (> 0) is the reorganization free energy; e is the electronic charge and χ the surface potential of the solution.

Dielectric dispersion of the solvent affects the solvation free energy $\Delta G_s(C)$ of the photon absorbing species C(aq). The following model is adopted:

The polarizability of the solvent molecules in the inner-sphere solvation shell of the solvated solute C(aq) absorbing a photon of energy E has the value α_w corresponding to the energy E. Conversely, the polarizability of solvent molecules in the outer-sphere solvation region of the solute is not affected by absorption of a photon by the solute. This polarizability retains the value α_w^0 corresponding to the limiting value ϵ_{op}^0 of the dielectric constant of the solvent in the visible range. The polarizability of the solvent molecules in both inner- and outer-sphere solvation regions of the species produced by photoionization of C(aq) has its usual value α_w^0 . Hence, the free energy of solvation $\Delta G_s(C^+)$ and the total free energy R for inner- and outer-sphere reorganization are not affected by dispersion. This model is reasonable since electron transfer also involves electronic reorganization of the solvent and these two processes cannot be separated sequentially.

The change of ΔG_m with the polarizability of the solvent therefore can be calculated from Eq. (1) by retaining in the expression for $\Delta G_s(C)$ only the terms depending on this polarizability. Thus,

$$\Delta G_m = A - U(ep_\alpha) - U(pp_\alpha) - U(p_\alpha p_\alpha) - U_{IND} - U_L(C,w) - U_L(w,w) - U_{REP}, \quad (2)$$

where A represents the sum of the terms of Eq. (1) except $-\Delta G_s(C)$, the contributions to $\Delta G_s(C)$ independent of the solvent polarizability and the free energy for Born charging of the outer-sphere solvation region. The U's in Eq. (2) are the energies for the following interactions and processes^{3,4}: $U(ep_\alpha)$ charge-induced dipole, $U(pp_\alpha)$ dipole-induced dipole, $U(p_\alpha p_\alpha)$ induced dipole-induced dipole, U_{IND} formation of induced dipoles, $U_L(C,w)$ solute-solvent London dispersion, $U_L(w,w)$ solvent-solvent London dispersion, U_{REP} solute-solvent and solvent-solvent Born repulsion. The quadrupole-induced dipole interaction energy is not included in Eq. (2) since it is negligible (ca. 0.01 eV).

Explicit forms of the energies in Eq. (2) are as follows^{3,4}:

$$U(ep_\alpha) = -Nze p_\alpha / r_0^2, \quad (3)$$

$$U(pp_\alpha) = 2bp p_\alpha / r_0^3 \quad (4)$$

$$U(p_\alpha p_\alpha) = bp_\alpha^2 / r_0^3, \quad (5)$$

$$U_{IND} = Np_\alpha^2 / 2\alpha_w. \quad (6)$$

$$U_L(C,w) = - (3N/2) [II_w / (I + I_w)] \alpha \alpha_w / r_0^6, \quad (7)$$

$$U_L(w,w) = - c I_w \alpha_w^2 / r_0^6, \quad (8)$$

$$U_{REP} = B - (1/x) \{ 2U(ep_\alpha) + 3[U(pp_\alpha) + U(p_\alpha p_\alpha)] + 6[U_L(C,w) + U_L(w,w)] \} \quad (9)$$

Notations are: N the number of water molecules in the inner-sphere hydration shell; z the absolute value of the ionic valence of species C(aq); p the dipole moment of the solvent; p_α the induced dipole moment; and r_0 the sum of the

crystallographic radii r_c of $C(aq)$ and r_w ($= 1.38 \text{ \AA}$) of the water molecule on the assumption that the center of the induced dipole is at the distance $r_c + r_w$ from the charge; I and I_w the ionization energies of $C(g)$ and the solvent, respectively, and α and α_w the corresponding polarizabilities; b a structure factor equal to 2.296 for tetrahedral coordination of water molecules in the inner-sphere shell and $b = 7.114$ for octahedral coordination; c the product of the numerical constant $3/4$ (from Eq. (7) for $I = I_w$) and a structure parameter, namely $c = 1.722$ and $c = 5.336$, respectively, for tetrahedral or octahedral coordination of water molecules in the inner-sphere shell (values of b and c in Ref. 3 and calculations in Ref. 4).

The Born repulsion energy U_{REP} of Eq. (9) is obtained^{3,4} by minimizing with respect to r_0 the sum of all the interaction energies involving the ionic charge, dipoles, induced dipoles, London dispersion. The term B in Eq. (9) represents the contribution independent of the solvent polarizability. The exponent x is such that U_{REP} is proportional to r_0^{-x} . The exponent x varies with the nature of the species involved over a range⁷ from 5 for He to 12 for Xe, Au^+ . Values of x from 8 to 10 applied to the cations studied in Ref. 3 and 4.

The induced dipole p_a is obtained^{3,4} by minimizing with respect to p_a the sum of the energies of Eqs. (3) to (6). Thus,

$$p_a = \alpha_w (Nze r_0 - 2bp) / (Nr_0^3 + 2b\alpha_w). \quad (10)$$

The second term in the denominator is rather small (10 to 20 percent) in comparison with the first term, and p_a is nearly proportional to α_w .

The change of the free energy of emission ΔG_m with the solvent polarizability can now be calculated from Eqs. (2) to (10). Results are displayed in Fig. 1 in which,

$$\Delta \Delta G_m = \Delta G_m(\alpha_w) - \Delta G_m(\alpha_w^0), \quad (11)$$

is the difference between the free energies of emission for the polarizability α_w and the limiting value $\alpha_w^0 (= 1.444 \times 10^{-24} \text{ cm}^3)$. The quantity ΔG_m varies almost linearly with α_w in Fig. 1, especially for $z = 1$. This is the case because ΔG_m of Eq. (2) can be written as

$$\Delta G_m = K_0 + K_1\alpha_w + K_2\alpha_w^2 + K_3\alpha_w^3, \quad (12)$$

if one takes p_a proportional to α_w , as is nearly the case (discussion of Eq. (10)). The K 's in Eq. (12) are independent of α and α_w , and the term $K_1\alpha_w$ is dominant for $z \neq 0$. Figure 1 shows that the effect of dispersion of the solvent on ΔG_m is significant for emission by aqueous solutions of ions and is far from negligible for solutions of molecules.

The calculation leading to Fig. 1 ($x = 9$) was repeated for the exponent x of Eq. (9) equal to 6 and 12. For instance, one calculates for $\alpha_w = 2.5 \times 10^{-24} \text{ cm}^3$: $\Delta G_m = 0.064$ and 0.116 eV for $z = 0$ and $x = 6$ and 12 , respectively; $\Delta G_m = 0.138$ and 0.271 eV for $z = 1$ and $x = 6$ and 12 , respectively. The quantity ΔG_m varies significantly with x because of the form of Eq. (9) for the Born repulsion energy U_{REP} .

B. Free energy of optical electron transfer as a function of photon energy

The relationship between polarizability and optical dielectric constant is needed for the analysis of experimental results on emission in Sec. IV. The polarizability α_w of liquid water is related to its refractive index at the photon energy E by the Lorenz-Lorentz equation,⁸

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)N_w\alpha_w, \quad (13)$$

where the number N_w of water molecules per unit volume is given by $N_w = \rho N_A / M$ (ρ the density of water, N_A Avogadro's number and M the molecular weight of water). It should be stressed that Eq. (13) allows the calculation of α_w from n^2 without correction for the difference between the actual internal field and the Lorentz field. The correction for this difference

appears in the relationship between the polarization and the field as shown in the Appendix. Equation (13) is valid for transparent and absorbing media, but the relationship between n and the optical dielectric constant ϵ_{op} is not the same: $\epsilon_{op} = n^2$ for transparent media; $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$ for absorbing media (k absorption coefficient; ϵ_1 and ϵ_2 real and imaginary parts of ϵ_{op} , respectively).

The change of free energy ΔG_m can now be computed as a function of photon energy E from Eqs. (2) to (11) and experimental data on n in Eq. (13). The values of n were used which were recently recalculated by Painter⁹ from the reflectance spectroscopy data in Ref. 10 and 11. The resulting plots for $z = 0$ and 1 resemble the plot¹⁰ of the real part of the dielectric constant against E . The ascending segments of the curves of Fig. 2 essentially correspond to normal dispersion of water and the descending segments to anomalous dispersion resulting from the two absorption bands of water with maxima at ca. 8.7 and 10.0 eV. The effect of dispersion on the energetics of optical electron transfer is significant since $\Delta G_m(\alpha_w)$ is higher than the limiting value $\Delta G_m(\alpha_w^0)$ by as much as ca. 0.3 eV. The shape of the curves in Fig. 2 is quite independent of the radius r_0 and is not affected significantly by the value of the exponent x in Eq. (9) and by the ionic valence z .

III. DISPERSION SPECTRA FOR OPTICAL ELECTRON TRANSFER

The effect of dielectric dispersion is investigated experimentally by measuring the yield Y for photoelectron emission by aqueous solutions as a function of photon energy E .¹ The yield (number of collected electrons per incident photon) is proportional to $(E - E_t)^s$ ($s = 2$ or $5/2$), where E_t is the threshold energy of the species in solution. One has $E_t = \Delta G_m$ to a good approximation,⁶ and consequently $dY^{1/s}/dE$ is proportional to $1 - d\Delta G_m/dE$,

that is, to $1 - d\Delta G_m/dE$, where $d\Delta G_m/dE$ varies with E because of dielectric dispersion. A dispersion spectrum is obtained¹ by plotting $dY^{1/5}/dE$ against E :

In the absence of dielectric dispersion, dispersion spectra would have the shape of a step function to a first approximation: $Y = 0$ and $dY^{1/5}/dE = 0$ for $E < E_t$; $dY^{1/5}/dE$ is constant ($\neq 0$) for $E > E_t$. Such a simple dispersion spectrum can be expected in the range of photon energies in which the change of free energy ΔG_m of Eq. (11) does not vary much with photon energy, namely for $E > 10$ eV (Fig. 2). The dispersion spectrum of water (Sec. IVC) is a good example of such a simple spectrum without major distortion from dispersion. Actually, the emission law is more involved than the simple proportionality of Y to $(E - E_t)^5$ in the vicinity of the threshold energy, and there is a progressive rise of $dY^{1/2}/dE$ with E over a few tenths of electronvolt beyond the threshold energy. This increase is not related to dispersion, and dispersion spectra therefore are examined in general at photon energies higher than the threshold energy by a few tenths of electronvolt.

Since $dY^{1/5}/dE$ is proportional to $1 - d\Delta G_m/dE$, that is, to $1 - d\Delta G_m/dE$, the quantity $-d\Delta G_m/dE$ was calculated as a function of the photon energy E for $z = 0$ and 1 (Fig. 3). Differentiation was performed by means of Savitsky-Golay convolutes as discussed in Ref. 1. The variations of the polarizability α of the solute with photon energy were not considered. The corresponding term (Eq. (7)) is small and the shape of the theoretical curve is hardly affected by variation of α . No correction of the curves of Fig. 3 was necessary for attenuation of the photon flux resulting from absorption in the layer of liquid from which photoelectrons are emitted. Such a correction is negligible for the absorption coefficient of liquid water⁹⁻¹¹ ($E < 11$ eV) within the thermalization length¹³ of low-energy quasifree electrons (20 to 40 Å).

IV. COMPARISON OF THEORY AND EXPERIMENTAL DISPERSION SPECTRA

A. Anions

Theory and experiment will be compared for the dispersion spectra of anions reported in Ref. 1 and for new spectra of different species. This comparison is made in Fig. 4 (curve A) for azide ion ($E_t \approx 7.4$ eV) which has a dispersion spectrum typical of inorganic anions. The curves A and C in Fig. 4 have the same general shape except that the maximum at 8.62 eV and minimum at 9.08 eV in the experimental spectrum A are much more pronounced than in the theoretical spectrum C. However, reflectance spectral analysis is particularly difficult in these regions because of the rapid variations of reflectance with photon energy and the resulting sensitivity of the relative peak heights to the smoothing and interpolation procedures. The photon energies at the extrema of the theoretical curve of Fig. 3 for $z = 1$ nevertheless agree very well with the corresponding average experimental photon energies for the 17 inorganic anions studied in Ref. 1 (Table I) with a mean deviation of only 0.06 eV. This is essentially the mean accuracy (0.04 eV) with which the extrema were located for all anions.

Agreement with theory is also achieved for ferrocyanide ion ($E_t = 6.2$ eV and 6.8 eV) which yields a dispersion spectrum (Fig. 4, curve B) similar to those of other inorganic anions. The ion is quite bulky ($r_c \approx 4.5$ Å) and the number N of water molecules in the first solvation shell certainly exceed the value $N = 6$ assumed in the construction of Fig. 3. Moreover, $z = 4$ (or 3 depending on the ionic equilibria in solution) and consequently the dispersion effect should be enhanced in comparison to the case of $N = 6$ and $z = 1$. This enhancement, however, is compensated by the higher radius $r_c \approx 4.5$ Å than the value $r_c \approx 2.0$ Å prevailing approximately for usual inorganic anions. The effect of dispersion for ferrocyanide ion therefore is similar in magnitude to the effect observed for uni- and divalent anions.¹

B. Cations

Results for cations are limited because emission by anions (Cl^-) interferes above ca. 8.6 eV and most cations have threshold energies above 7 eV. The dispersion spectra for V^{2+} ($E_t = 6.8$ eV) and Cr^{2+} ($E_t = 7.0$ eV) in Fig. 5 (curves A and B) are remarkably similar and exhibit the same features as the theoretical curve. The magnitude of the dispersion effect for these cations is comparable to the effect observed with anions ($z = 1$ or 2) having crystallographic radii r_c of the order of 2 \AA although the radii of V^{2+} (0.88 \AA) and Cr^{2+} (0.84 \AA) are much shorter than for anions.

Complexation with chloride probably accounts for the magnitude of the dispersion effect since the crystallographic radius of species such as VCl^+ and CrCl^+ is comparable to that of anions.

C. Molecules

Water ($E_t = 10.04 \pm 0.02 \text{ eV}^{14}$) has a dispersion spectrum (Fig. 6) which very approximately resembles the step function expected in the absence of dispersion for an emission yield proportional to $(E - E_t)^{1/2}$ (Sec. III). This is the case because $-d\Delta G_m/dE$ does not vary markedly with photon energy in the 10.3 to 11 eV range (Fig. 3). Excellent plots of $\gamma^{1/2}$ against photon energy are indeed obtained¹⁴ for water as one expects for a free energy ΔG_m nearly independent of E in the range covered by such plots. The spectrum of Fig. 6 exhibits the usual maximum near 9.88 eV (Table I) below the extrapolated threshold energy in a range of photon energies in which the emission yield is very low. The maxima at 10.33 and 10.69 eV and the minimum at 10.55 eV predicted by theory (Fig. 3) are indeed observed (Table I).

The dispersion spectra of aqueous solutions of organic molecules are also accounted for by the present theory. Results are shown in Fig. 7 for aniline ($E_t \approx 7.3$ eV, curve A), hydroquinone ($E_t \approx 7.1$ eV, curve P) and phenol

($E_t \approx 7.6$ eV, curve C). These substances exhibit (< 11 eV) two ionization bands in the gas phase. The second threshold energies in solution are ca. 8.5, 8.0 and 8.3 eV on the assumption that the energy difference between the two bands in the same for the gas phase^{15,16} and solution.

The second transition band accounts for the difference between the experimental (curves A, B, C) and theoretical (curve D) spectra in Fig. 7. Thus, $dY^{1/2}/dE$ for aniline (curve A) increases in the 8.5 to 8.95 eV range because of the second transition. A maximum is reached at 8.95 eV because the dispersion effect becomes dominant, and the expected minimum at 9.08 eV (Table I) is observed. The same interpretation applies to hydroquinone (curve B). The derivative $dY^{1/2}/dE$ increases above the second threshold energy (ca. 8.0 eV), but dispersion already shows up in the maxima near 8.17 and 8.66 eV (Table I). The minimum near 9.08 eV expected from dispersion is well defined. Phenol (curve C) displays the increase of $dY^{1/2}/dE$ beyond the second threshold energy ($E_t \approx 8.3$ eV) expected from the second transition, but dispersion soon becomes dominant as shown by the maximum near 8.66 eV (Table I) and the rather sharp drop to the usual maximum near 9.08 eV. The three spectra of Fig. 7, it is concluded, do not present any unusual feature not accounted for by the present theory once the complication arising from two consecutive transitions is recognized.

CONCLUSION

The effect of dielectric dispersion of the solvent on the energetics of optical electron transfer is understood quantitatively in its essential aspects, and the theory thus developed agrees with experiment. The study of the dispersion effect provides a unique way of investigating experimentally the change of solvation free energy resulting from variation of the polarizability of the solvent at constant nuclear configuration of the solvation shell.

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APPENDIX

The molar polarization with correction for the difference between the Lorentz and internal fields is⁸

$$[(n^2 - 1)/(n^2 + 2)](M/\delta) = (4\pi/3)N_A\alpha_w G, \quad (14)$$

where the notations are the same as in Eq. (13) and the correction function is

$$G = 9\epsilon_{op}/(n^2 + 2)[(2n^2 + 1) - (\alpha_w/a^3)(2n^2 - 2)], \quad (15)$$

the radius a being such that $a^3 = (3/4\pi)M/N_A\delta$. Solving Eqs. (14) and (15) for α_w , one obtains

$$\alpha_w = (3/4\pi)(1/N_A)(n^2 - 1)(2n^2 + 1)/[9n^2 + (n^2 - 1)(2n^2 - 2)]. \quad (16)$$

The denominator is equal to $(n^2 + 2)(2n^2 + 1)$, and the resulting value of α_w is that given by the Lorenz-Lorentz equation of Eq. (13).

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TABLE I. Photon energies at the extrema of dispersion spectra: theory vs. experimental results

Extremum	Theory ^a (eV)	Experiment ^b (eV)
min	7.45	7.58 (0.02)
max	8.17	8.16 (0.06)
max	8.66	8.65 (0.03)
min	9.08	9.11 (0.03)
max	9.30	9.37 (0.06)
min	9.40	9.63 (0.02)
max	9.88	9.86 (0.04)
max	10.33	10.35
min	10.55	10.50
max	10.69	10.68

^aPhoton energies from Fig. 3 ($z = 1$). Maximum at 8.66 eV definitely indicated by the numerical values of $-d\Delta G_m/dE$ calculated at 0.01 eV intervals.

^bValues below 10 eV are average photon energies for 17 inorganic anions from Ref. 1; standard deviation between parentheses. Values above 10 eV for water (Sec. IVC and Fig. 6).

List of Captions

Fig. 1. Variations of the change of free energy $\Delta\Delta G_m$ of Eq. (11) with the polarizability α_w of the solvent for $z = 0$ and 1. Data: $r_c = 2 \text{ \AA}$, $N = 6$, $p = 1.834 \text{ debye}$,⁵ $\alpha = 3 \times 10^{-24} \text{ cm}^3$, $I = 4 \text{ eV}$, $I_w = 12.6 \text{ eV}$, $x = 9$.

Fig. 2. Variations of the change of free energy $\Delta\Delta G_m$ of Eq. (11) with photon energy for $z = 0$ and 1. Values of $\Delta\Delta G_m$ for the values of α_w computed from Eq. (13) for the data on the refractive index n of water from Painter.⁹

Fig. 3. Variations of $-d\Delta\Delta G_m/dE$ with photon energy E for $z = 0$ and 1. Same data as for Fig. 1. Photon energies indicated at the extrema of the curve for $z = 1$ are also valid for $z = 0$.

Fig. 4. Dispersion spectra of 1 M sodium azide (A) and 0.05 M potassium ferrocyanide (B) in aqueous solution compared with the variations of $-d\Delta\Delta G_m/dE$ with photon energy (C) of Fig. 3 for $z = 1$.

Fig. 5. Dispersion spectra of 0.5 M VCl_2 (A) and 1 M CrCl_2 (B) in aqueous solution compared with the variations of $-d\Delta\Delta G_m/dE$ with photon energy (C) of Fig. 3 for $z = 1$.

Fig. 6. Dispersion spectrum of water.

Fig. 7. Dispersion spectra of 0.01 M aniline (A), 0.05 M hydroquinone (B) and 0.1 M phenol (C) in aqueous solution compared with the variations of $-d\Delta\Delta G_m/dE$ with photon energy (D) of Fig. 3 for $z = 0$.

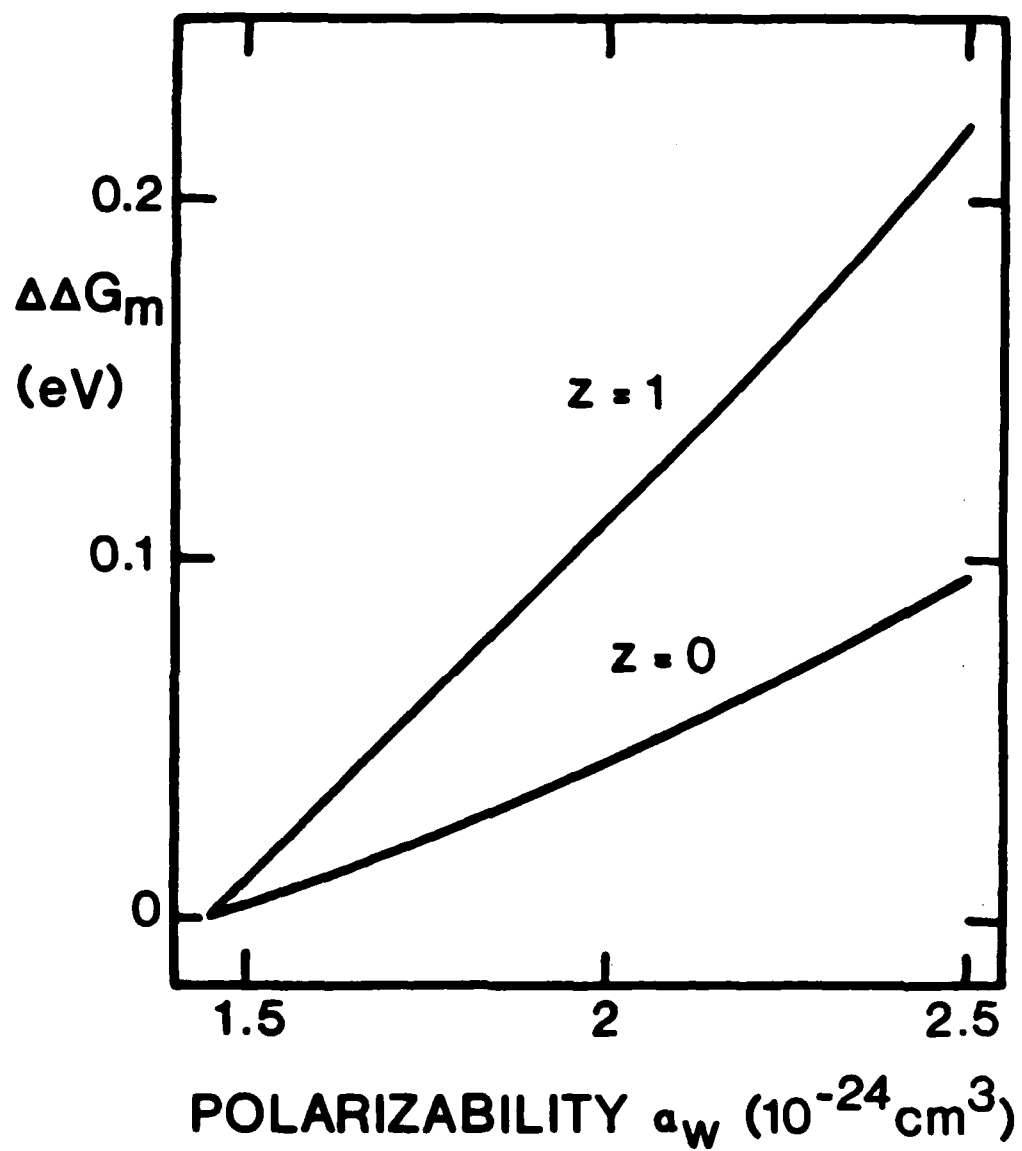


FIG. 1

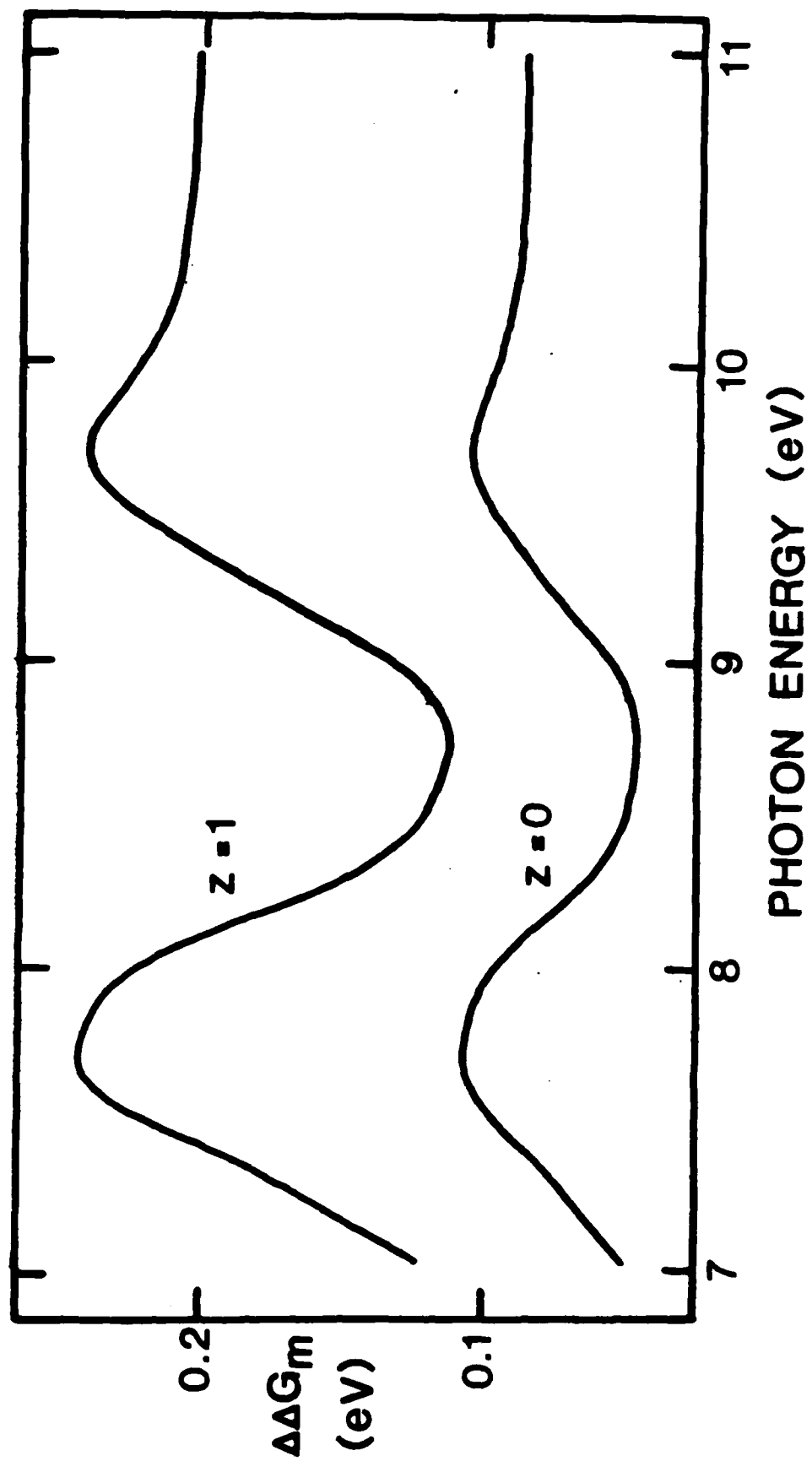


FIG. 2

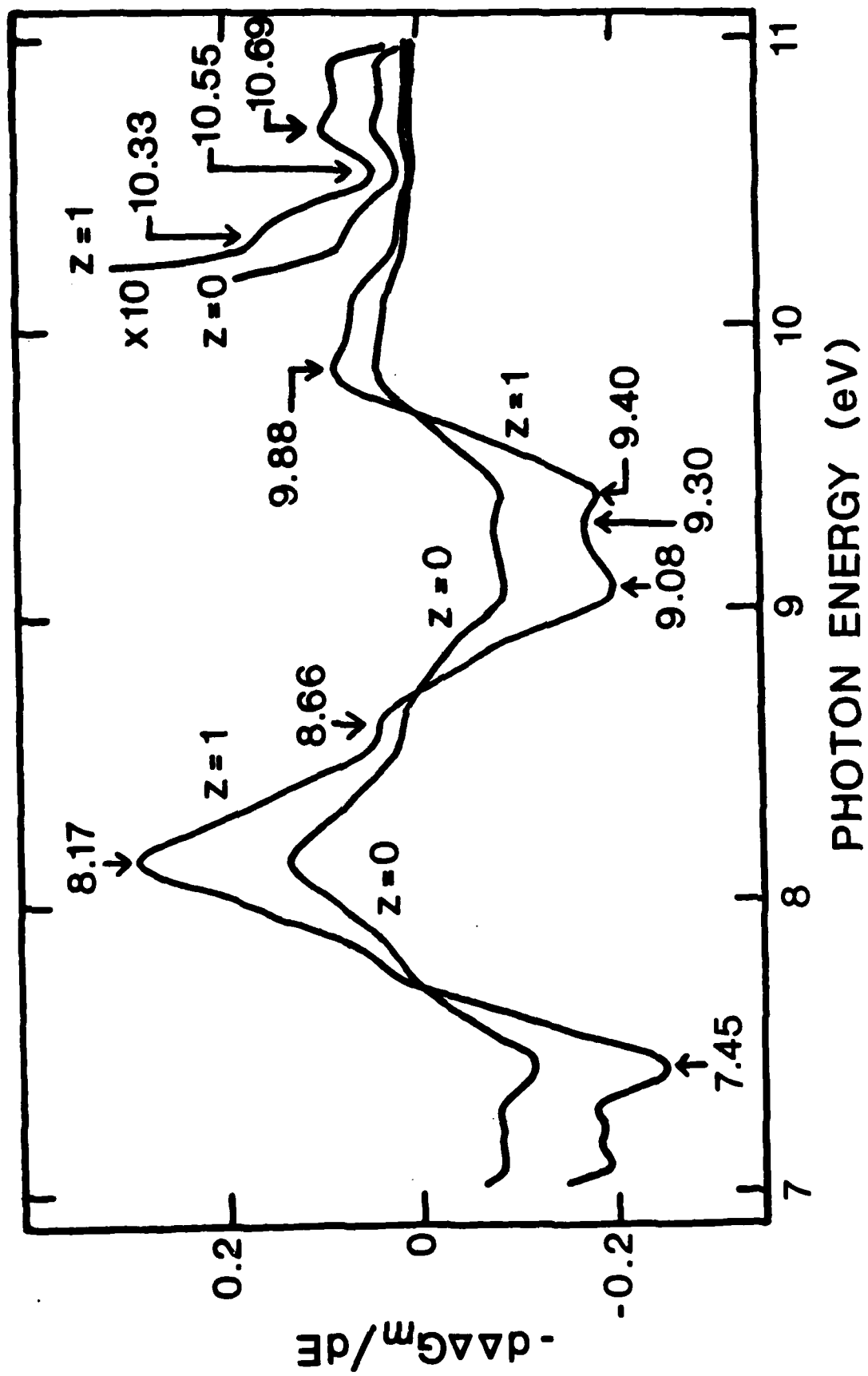


FIG. 3

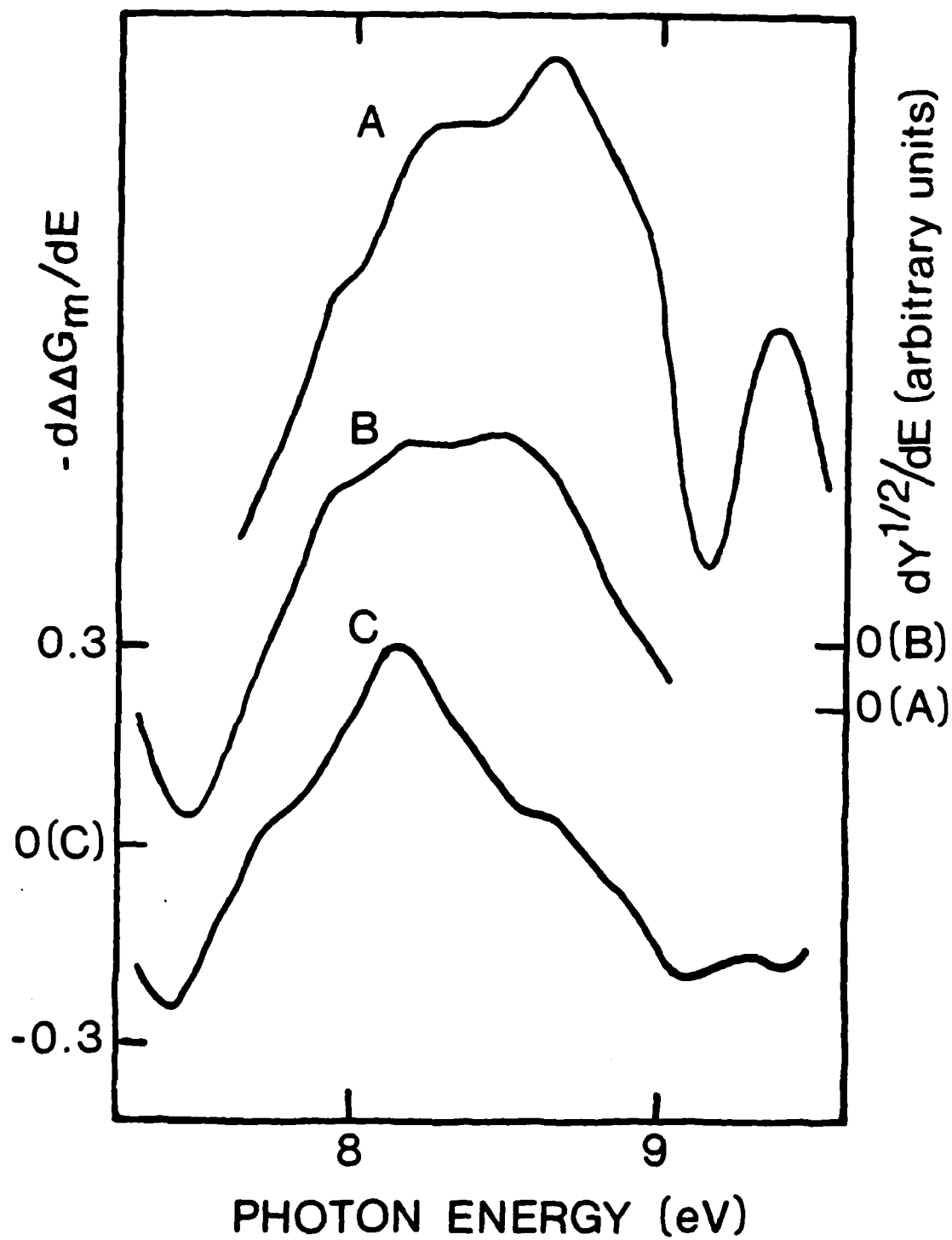


FIG. 4

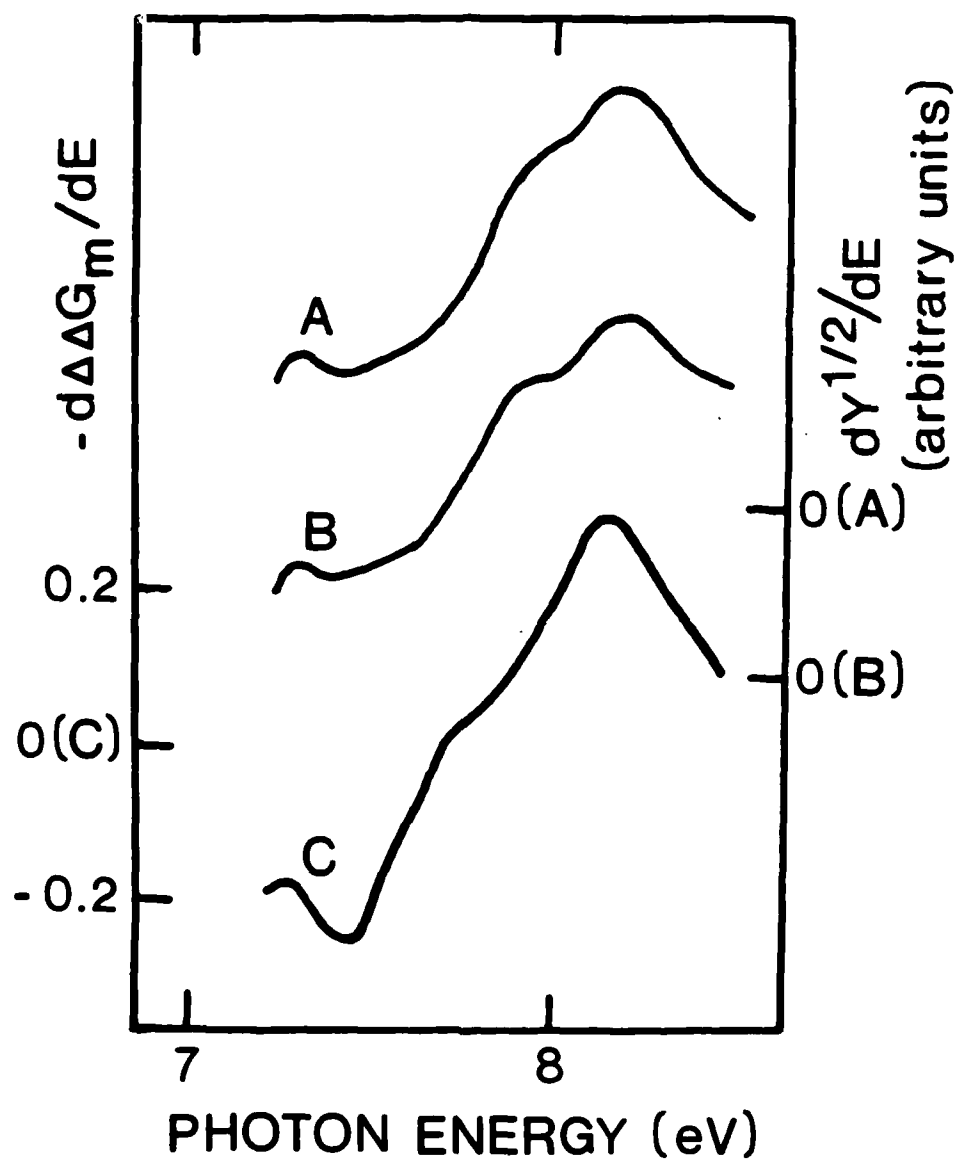


FIG. 5

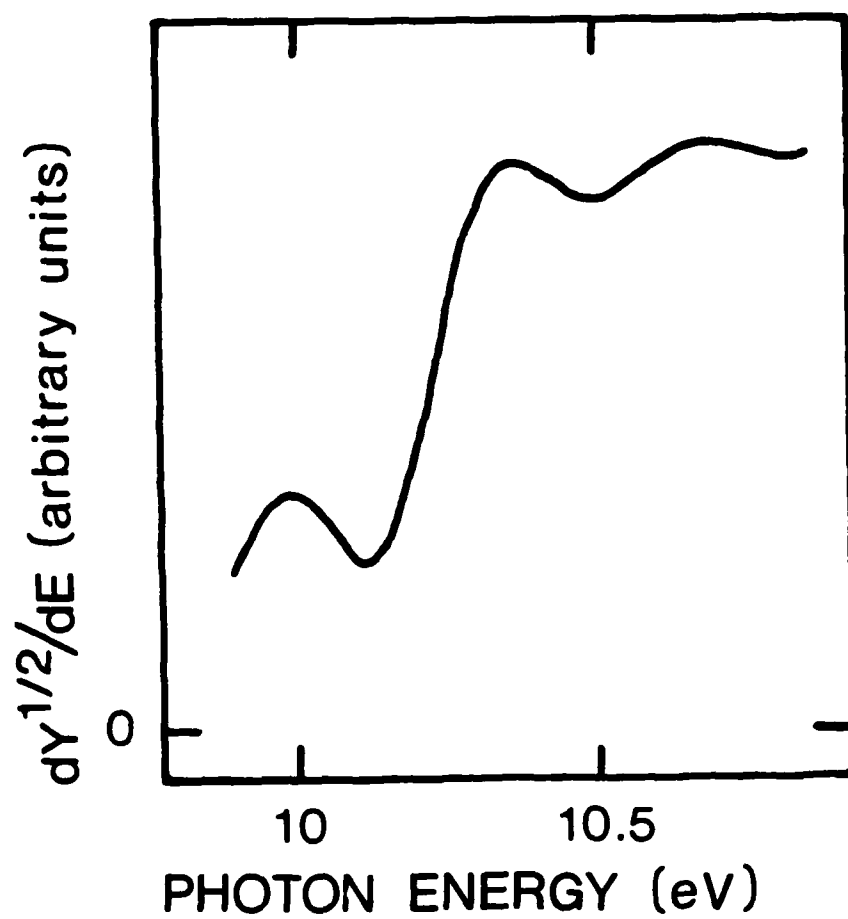


FIG. 6

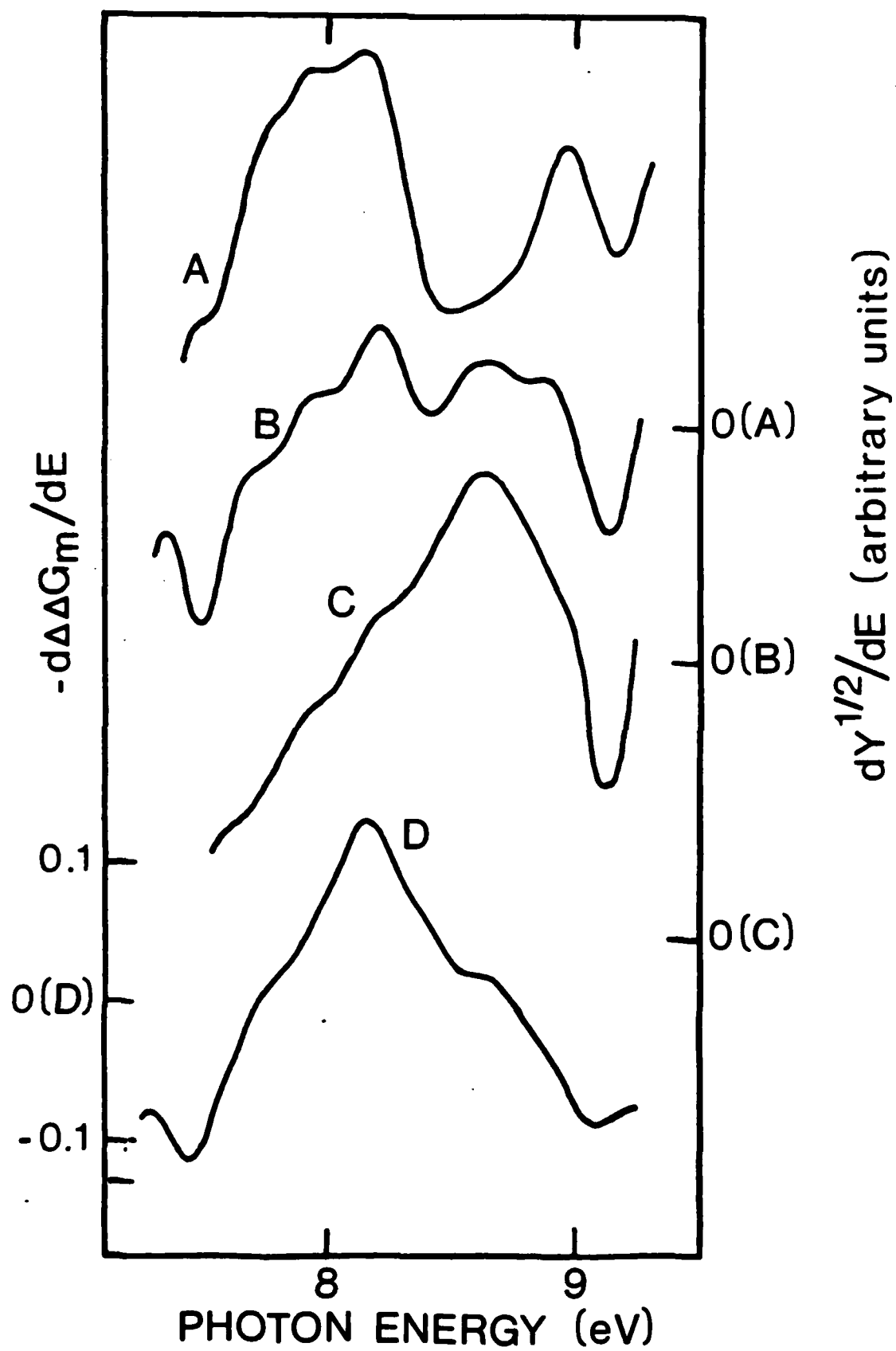


FIG. 7

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